

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 072 647 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
31.01.2001 Bulletin 2001/05

(51) Int. Cl.⁷: **C08L 63/02**, **C08J 9/10**,
B32B 5/18

(21) Application number: **00109812.8**

(22) Date of filing: **09.05.2000**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• **Kim, Jin Soo**
Book-ku, Ulsan (KR)
• **Ju, Hu Ryeong**
Daewol-myun, Icheon, Kyongki-do (KR)

(30) Priority: **30.07.1999 KR 9931309**

(74) Representative:
TER MEER STEINMEISTER & PARTNER GbR
Patentanwälte,
Mauerkircherstrasse 45
81679 München (DE)

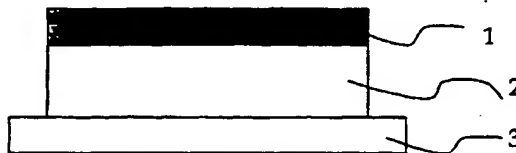
(71) Applicants:
• **HYUNDAI MOTOR COMPANY**
Chongro-ku, Seoul 110-793 (KR)
• **Hong Seong Chemical Co., Ltd.**
Kangnam-ku, Seoul (KR)

(54) **Expandable reinforcing sheet material for vehicle outer panel**

(57) Expandable reinforcing sheet material for vehicle outer panel, comprising nitrile butadiene rubber (NBR) modified epoxy resin, bisphenol A type epoxy resin, potassium-zincs thermal stabilizer, calcium carbonate, polyvinyl chloride, carbon black, azodicarbonamides expanding agent, expanding accelerator, adhesion supplying agent, and dicyandiamide, provides

excellent adhesion ability to the outer panel of the vehicle, good workability, vibration damping capacity can be suitable for applying to the outer panel of vehicle and thus the outer panel of vehicle on the backside of which the reinforcing material is attached can become lighter and thinner.

Fig. 1



EP 1 072 647 A2

Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to expandable reinforcing sheet material, particularly expandable reinforcing sheet material for vehicle outer panel comprising nitrile butadiene rubber modified epoxy resin, bisphenol A type epoxy resin, heat stabilizer, expansion agent, expansion accelerator, adhesion providing agent, heat activation type hardener, and filler, which can be expanded by heat and the gravity thereof can be reduced. The expandable reinforcing sheet material has excellent adhesion ability to the outer panel of the vehicle, good workability, vibration damping capacity
 10 can be suitable for applying to the outer panel of vehicle. The outer panel of vehicle on the backside of which the reinforcing material is attached can become lighter and thinner.

BACKGROUND OF THE INVENTION

15 [0002] In vehicles, use of thinner panels has been required for saving energy. This results in reduced strength, which causes automobiles insufficient surface tensional rigidity and insufficient solid appearance.

[0003] In order to solve the problems, there were proposed various processes for producing a vehicle outer panel structure having lightweightness. For example in the laid open of Japanese Patent Application No 1988-272515, there was proposed a process which comprises attaching to the backside of a panel sheet material having a three layer structure consisting a first layer which is a foamable composition comprising as essential component, a vinyl chloride resin,
 20 a plasticizer, a high temperature decomposition type expansion agent, an epoxy resin and a heat activation type hardener for epoxy resin, a second layer which is a cloth, and a third layer which is a thin metal film, and then heating the resulting panel to allow the sheet material to give resin to expand and hardening.

[0004] In this process, however, the foamable composition contains a vinyl chloride resin as a thermoplastic resin, and therefore has poor adhesion to oily surface and, when heated to give rise to expand and hardening, gives a sheet of poor heat resistance.

[0005] Hence, the process is applicable to vehicle outer panels after electro deposition but inapplicable to vehicle outer panels before electro deposition.

[0006] In the automobile industry, attaching of reinforcing sheet material to vehicle outer panel before electro deposition is strongly desired for higher productivity or for use of such a reinforcing sheet material to as many applications as possible.

[0007] Especially, the reinforcing material for the quarter panel part and the door fender panel of vehicles uses a stainless steel or a fiber glass as the restraint layer, and an unexpandable pad is adhered to the backside of the restraint layer with the thickness of 1.5 ~ 2.5 mm. And finally a releasing paper is covered on the unexpandable type pad to protect the unexpandable pad.
 35

[0008] That is, since the quarter panel and the door fender panel of the vehicle have the curved shape, the expandable pad is used as the reinforcing sheet material of the curved portion of vehicle. Then the reinforcing sheet material for the quarter panel and the door fender panel is separated partially after electro deposition. And water or a foreign substance is inserted into the gap between the panel and the reinforcing sheet, which causes the panel of the vehicle to get rust.
 40

[0009] On the other hand, in order to solve the problem the glass wool is used as the restraint layer, the glass wool also cannot give a sufficient solution.

SUMMARY OF THE INVENTION

45 [0010] The object of the present invention is to provide expandable reinforcing sheet material for curved outer panel of vehicle comprising a nitrile butadiene rubber used as basic material and polyvinyl chloride, and having excellent adhesion to the outer panel of the vehicle, good workability, vibration damping capacity.

[0011] The other object of the present invention is to provide a reinforcing sheet comprising the reinforcing sheet material above described become lighter and thicker.

50 [0012] The present invention to achieve the above object comprises expandable reinforcing sheet material for vehicle outer panel comprising nitrile butadiene rubber (NBR) modified epoxy resin, bisphenol A type epoxy resin, potassium-zinc thermal stabilizer, calcium carbonate, polyvinyl chloride, carbon black, azodicarbonamides expanding agent, expanding accelerator, adhesion providing agent, and dicyandiamide. This reinforcing sheet material has high
 55 ratio of expansion and the outer panel of vehicle to which the reinforcing sheet material become lighter and thinner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The above object and other advantages of the present invention will become more apparent by describing in detail the preferred embodiment of the present invention with reference to the attached drawings in which:

5

FIG 1 is a section view of the reinforcing sheet comprising an expandable reinforcing sheet material, a restraint layer for restraining the reinforcing sheet material, and a releasing paper for covering the reinforcing sheet material in accordance with the present invention

10 DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0014] The expandable reinforcing sheet material in accordance with the present invention comprises 10 ~ 14 weight % of nitrile butadiene rubber (NBR) modified epoxy resin alone or nitrile butadiene rubber (NBR) modified epoxy resin mixed with another modified epoxy resin selected from the group consisting of carboxyl terminated butadiene acrylonitrile polymer (CTBN), amine terminated butadiene acrylonitrile polymer (ATBN) and methacrylate vinyl terminated butadiene acrylonitrile polymer (VTBN), 5 ~ 20 weight % of bisphenol A type epoxy resin, 0.3 ~ 4 weight % of potassium-zincs thermal stabilizer, 17 ~ 30 weight % of calcium carbonate, 10 ~ 20 weight % of polyvinyl chloride, 1 ~ 2 weight % of carbon black, 3 ~ 5 weight % of azodicarbonamides expanding agent, 0.3 ~ 2 weight % of expanding accelerator, and 4 ~ 7 weight % of adhesion providing agent, 0.1 ~ 2 weight % of dicyandiamide.

[0015] The expandable reinforcing sheet material comprising the above materials has excellent adhesion to the oily steel panel of vehicle. The reinforcing sheet material is expanded and hardened by heat and tightly adheres to the surface of the oily panel. And the reinforcing sheet material in accordance with the present invention is expanded in about 100 % or more of its original volume and has excellent reinforcing capacity and the vibration damping capacity.

[0016] The expandable reinforcing sheet material in accordance with the present invention comprises NBR modified epoxy resin, bisphenol A type epoxy resin, thermal stabilizer, filler having calcium carbonate, polyvinyl chloride, carbon black, expansion agent, expansion accelerator, adhesion providing agent, and inclosed type hardener.

[0017] 10 ~ 14 weight % of the NBR modified epoxy resin alone or nitrile butadiene rubber (NBR) modified epoxy resin mixed with another modified epoxy resin selected from the group consisting of carboxyl terminated butadiene acrylonitrile polymer (CTBN), amine terminated butadiene acrylonitrile polymer (ATBN) and methacrylate vinyl terminated butadiene acrylonitrile polymer (VTBN) and 5 ~ 20 weight % of the bisphenol A type epoxy resin are used in order to supply the adhesion strength and impact resistance capacity. Then if the amount of the NBR modified epoxy resin used is out of the above range, it is not preferred because there are problems in the separation of the reinforcing sheet and the impact resistance capacity.

[0018] And if the bisphenol A type epoxy is less than 5 weight %, the adhesion capacity of the reinforcing sheet material in accordance with the present invention become low. Whereas the amount of the bisphenol A type epoxy resin is excess 20 weight %, the adhesion strength is increase that causes problems about separation and crack in the reinforcing sheet material in accordance with the present invention.

[0019] The potassium-zincs thermal stabilizer is used to increase the thermal stability. Then if the amount of the potassium-zincs thermal stabilizer is less than 0.3 weight %, the thermal resistance capacity is decreased. Whereas the amount of the potassium-zincs thermal stabilizer is excess 4-weight %, the adhesion capacity and the storage stability are decreased.

[0020] The calcium carbonate is used as filler that give rise volume of the reinforcing sheet in accordance with the present invention. Then if the amount of the calcium carbonate is out of the above range, it is difficult that volume of the reinforcing sheet is maintained, and workability and the adhesion ability are decreased.

[0021] The polyvinyl chloride is used in order to give expansion capacity to the reinforcing sheet material in accordance with the present invention. Then if the amount of the polyvinyl chloride is less than 10 weight %, the heat resistance ability is decreased. Whereas if the amount of the polyvinyl chloride is excess 20 weight %, the expansion ability and adhesion strength are increased but thermal resistance is decreased and ageing is promoted.

[0022] The carbon black is used in order to give coloration and rigidity. Then if the amount of the carbon black is out of the above range, the rigidity is decreased or is exceeded.

[0023] The azodicarbonamides expansion agent is used in order to give expansion ability to the reinforcing sheet in accordance with the present invention. Then if the azodicarbonamides expansion agent is less than 0.3 weight %, there is a problem that the reinforcing sheet material is not expanded because the decomposition temperature of the expansion agent is not lowed. Whereas if the amount of the azodicarbonamides expansion agent is excess 2 weight %, the residual reactant restricts the expansion rate and the expansion form of the reinforcing sheet material in accordance with the present invention.

[0024] The expansion accelerator is selectively used between ZnO and Zn-St.

[0025] The expansion rate of the reinforcing sheet material in accordance with the present invention is 150 ~ 200

% of its original volume.

[0026] 4 ~ 7 weight % of the adhesion agent is used in order to provide the adhesion ability and the workability to the reinforcing sheet. Then if amount of the adhesion agent is less than 4 weight %, the workability is decreased. Whereas if the amount of the adhesion agent exceeds 7 weight %, workability and initial adhesion ability become low.

5 [0027] The adhesion agent can be prepared by kneading monomeric interpolymerization resin (K-value 50 or thereabout), interpolymerization resin (PVC) of 50 ~ 100 μm in grain size, and DOP(dioctyl phthalate) and DOA (dioctyl adipate) that are the mixed plasticizer using a known kneader such as planetary mixer, kneader, roller or the like.

[0028] The present invention can use 0.1 ~ 2 weight % of dicyandiamide as hardener in order to prevent the prompt decreasing of the penetration degree on storage the reinforcing sheet material at the normal temperature. Then, if the
10 amount of the dicyandiamide is less than 0.1 weight %, the hardening operation is not completely done and the hardness and the adhesion strength become low. Whereas if the amount of the dicyandiamide exceeds 2 weight %, the separation ability of the adhesion surface and the invasion ability of the storage stability are decreased.

[0029] The reinforcing sheet material in accordance with the present invention is prepared by the following method.

[0030] Fig 1 shows the partial cross-section of the reinforcing sheet assembly in accordance with the present invention.
15 An expandable reinforcing sheet 2 is made of the expandable resin composition prepared by the composition described above, which is extruded by an extruding machine and pass through between two rolls to be a certain thickness.

[0031] A restraint layer 1 is attached on the one surface of the expandable sheet 2 and a releasing paper 3 is attached on the other surface of the expandable sheet 2. The sheet assembly is continuously prepared and cut to a certain size by a cutter to be a proper size adapted to the curved outer panel of the vehicle.
20

[0032] The expandable sheet 2 is expanded by heating at 150 ~ 190 °C of temperature for 15 ~ 40 minutes that is condition of the electro deposition of the vehicle assembling line and can have excellent adhesion ability to the curved outer panel of the vehicle.

[0033] Therefore, the expandable reinforcing sheet material in accordance with the present invention is suitably used for reinforcement of metal panel before electro deposition in particular.
25

[0034] Hereafter, the expandable reinforcing sheet material is described in more detail by the examples.

PRACTICE EXAMPLE

30 [0035] The practice example of the expandable sheet material that comprises the composition and the amount listed in table 1 is prepared.

[0036] NBR modified epoxy resin, bisphenol A type epoxy resin, thermal stabilizer, polyvinyl chloride, carbon black, expansion agent and expansion accelerator are inserted into the kneader.

[0037] Next, the adhesion agent is prepared by melting the monomeric interpolymerization resin of vinyl acetate and vinyl chloride into the mixed plasticizer. And a reinforcing composition is prepared by additionally input into the prepared adhesion agent above into the kneader and dicyandiamide is input and mixed by the kneader or high speed mixer.
35

[0038] The reinforcing composition is extruded by the extrusion machine, and the reinforcing sheet in accordance with the present invention is prepared. Then the glass fiber is attached on the one surface of the expandable sheet 2 and the releasing paper is attached on the other surface of the expandable sheet 2.
40

TEST EXAMPLE

[0039] The test example of the expandable sheet 2 is prepared using the practice example described above.

45 [0040] At 20 °C of temperature, the restraint layer 1 comprising stainless or glass wool is attached on the one surface of the expandable sheet 2 of which color is gray color or black, and the releasing paper 3 is attached on the other surface of the reinforcing material 2. As the result of that, the reinforcing sheet for vehicle outer panel in accordance with the present invention is prepared.

[0041] Next, the releasing paper is removed, and the surface of the expandable sheet 2 is attached on the backside of the outer panel of vehicle. The expandable sheet 2 attached on the backside of the outer panel of vehicle is heated at 170 °C of temperature for 30 minutes. Then the expandable material 2 is naturally expanded, adhered and finally hardened.
50

[0042] Herewith, the test for the ratio of the expansion is carried out by the method according to KS M 2095 10 article.
55

TABLE 1

Classification		Contents
Component of Composition	NBR modified epoxy resin	14
	Bisphenol A type epoxy resin	19
	PVC	18.5
	Filler	29
	Thermal stabilizer	3.8
	Adhesion agent	7
	Carbon black	2
	Expansion agent	4
	Expansion accelerator	1.2
	Latent hardener (dicyandiamide)	1.5
	Ratio of expansion (%)	170
Physical properties	Thickness (mm)	1.0
	Weight (g)	125

[0043] As is clear from the table 1, the reinforcing sheet materials for vehicle outer panel in accordance with the present invention have excellent adhesion ability. And outer panel of vehicle having the reinforcing sheet become lighter and thinner.

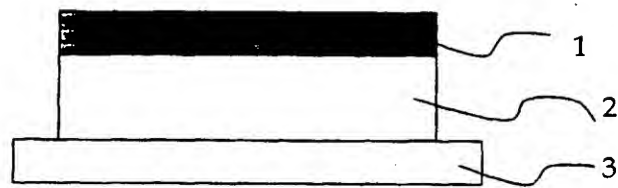
Claims

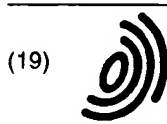
1. Expandable reinforcing sheet material comprising:

10 ~ 14 weight % of nitrile butadiene rubber (NBR) modified epoxy resin alone or nitrile butadiene rubber (NBR) modified epoxy resin mixed with another modified epoxy resin selected from the group consisting of carboxyl terminated butadiene acrylonitrile polymer (CTBN), amine terminated butadiene acrylonitrile polymer (ATBN) and methacrylate vinyl terminated butadiene acrylonitrile polymer (VTBN),
 5 ~ 20 weight % of bisphenol A type epoxy resin,
 0.3 ~ 4 weight % of potassium-zincs thermal stabilizer,
 17 ~ 30 weight % of calcium carbonate,
 10 ~ 20 weight % of polyvinyl chloride,
 1 ~ 2 weight % of carbon black,
 3 ~ 5 weight % of azodicarbonamides expanding agent,
 0.3 ~ 2 weight % of expanding accelerator,
 4 ~ 7 weight % of adhesion providing agent, and
 0.1 ~ 2 weight % of dicyandiamide.

2. Expandable reinforcing sheet comprising the reinforcing sheet material prepared by the claim 1, a restraint matter selected between a stainless steel and glass wool attached on one surface of the reinforcing sheet material, and a releasing paper attached on the other surface of the reinforcing sheet material.

Fig. 1





Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 072 647 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
04.10.2001 Bulletin 2001/40

(51) Int Cl.7: **C08L 63/02, C08J 9/10,
B32B 5/18**

(43) Date of publication A2:
31.01.2001 Bulletin 2001/05

(21) Application number: **00109812.8**

(22) Date of filing: **09.05.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Kim, Jin Soo
Book-ku, Ulsan (KR)
• Ju, Hu Ryeong
Daewol-myun, Icheon, Kyoungki-do (KR)

(30) Priority: **30.07.1999 KR 9931309**

(74) Representative:
TER MEER STEINMEISTER & PARTNER GbR
Patentanwälte,
Mauerkircherstrasse 45
81679 München (DE)

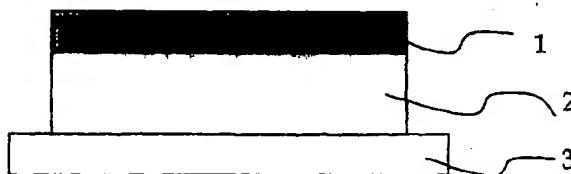
(71) Applicants:
• **HYUNDAI MOTOR COMPANY**
Chongro-ku, Seoul 110-793 (KR)
• **Hong Seong Chemical Co., Ltd.**
Kangnam-ku, Seoul (KR)

(54) **Expandable reinforcing sheet material for vehicle outer panel**

(57) Expandable reinforcing sheet material for vehicle outer panel, comprising nitrile butadiene rubber (NBR) modified epoxy resin, bisphenol A type epoxy resin, potassium-zinc thermal stabilizer, calcium carbonate, polyvinyl chloride, carbon black, azodicarbonates expanding agent, expanding accelerator, adhesion

supplying agent, and dicyandiamide, provides excellent adhesion ability to the outer panel of the vehicle, good workability, vibration damping capacity can be suitable for applying to the outer panel of vehicle and thus the outer panel of vehicle on the backside of which the reinforcing material is attached can become lighter and thinner.

Fig. 1



EP 1 072 647 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 10 9812

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 513 737 A (NIPPON ZEON CO ;ZEON KASEI KK (JP)) 19 November 1992 (1992-11-19) * page 2, line 38 - page 5, line 37 * * example C; table 1 * ---	1,2	C08L63/02 C08J9/10 B32B5/18
A	EP 0 518 253 A (NIPPON ZEON CO) 16 December 1992 (1992-12-16) * page 2, line 45 - page 5, line 45 * * example 7; table 1 * ---	1,2	
D,A	US 4 830 908 A (KOBAYASHI TAKEO ET AL) 16 May 1989 (1989-05-16) * column 2, line 8 - line 67 * * examples 1,7; tables 1A,2 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08L C08J B32B B62D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 August 2001	Examiner Neugebauer, U
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

EP 00 10 9812 (PC) 01

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 10 9812

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-08-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0513737 A	19-11-1992	JP 2940720 B	25-08-1999
		JP 4336240 A	24-11-1992
		US 5271612 A	21-12-1993
EP 0518253 A	16-12-1992	JP 4364937 A	17-12-1992
		JP 6069739 B	07-09-1994
		DE 69219403 D	05-06-1997
		DE 69219403 T	21-08-1997
		US 5198286 A	30-03-1993
US 4830908 A	16-05-1989	JP 1803896 C	26-11-1993
		JP 5011527 B	15-02-1993
		JP 63272515 A	10-11-1988

EPC FORM P-452

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)